

## NOTE

## Effect of Collision Efficiency on the Evolution of the Surface of Diffusion-Limited Deposits

**The effect of the collision efficiency of particles deposited onto a rough substrate and the evolution of the deposit profile were investigated using 2D on-lattice Monte Carlo simulations. The case of a diffusive long-range transport regime as representative of the colloidal deposition from the suspended phase was considered. The initial profile of the substrate was modeled as a sinusoidal wave. The decay of the initial profile in the course of deposition was monitored by a decrease in the Fourier amplitude  $A_w$  corresponding to the wavelength of the initial roughness. The best “memory” of the deposit, i.e., the slowest decay of  $A_w$ , was found to correspond to intermediate values ( $\sim 0.1$ ) of the collision efficiency.** © 2001 Academic Press

**Key Words:** particle deposition; collision efficiency; substrate roughness; roughness evolution.

## INTRODUCTION

There is a growing evidence that the morphology of colloidal deposits can be predicted from properties of particles with respect to transport to the surface and by close-range chemical particle–particle and particle–surface interactions (1, 2). Yet another factor that may be important for and, in some cases, have a dominant influence on the morphology of deposits is the profile of the underlying substrate onto which the deposition occurs. The “memory” of a depositing layer with respect to the substrate has important implications for applications such as membrane production and thin layer deposition as well as for controlling undesirable deposition on rough surfaces, colloidal fouling of membranes, and scaling in water pipes.

A considerable amount of research aimed at understanding the growth and resulting microstructure of films produced during chemical vapor deposition has been carried out recently (3–5). Singh and Shaqfeh developed a model (3) that includes surface reemission in the study of the evolution of rough surfaces in low-pressure chemical vapor deposition. They studied the microstructure of a ballistically deposited (Knudsen number  $\gg 1$ ) film formed at different values of collision efficiency  $\alpha$  and showed that two different mechanisms—cusp and keyhole formation—caused the decay of surface roughness for  $\alpha > 0$  and  $\alpha > 1$  limits, correspondingly. At the critical value of collision efficiency  $\alpha_c = 0.45$ , a transition between these two mechanisms was observed.

The changes in deposit morphology induced by variations in collision efficiency differ from those induced by changes in long-range transport. In the former case, a decrease in  $\alpha$  results in a thickening of the deposit branches, which is in sharp contrast with the latter case where an increasingly ballistic character of deposition leads to formation of an increasingly dense web-like structure, more homogeneously distributed in space (6). This consideration has motivated the study presented here in which Monte Carlo simulations of diffusion-limited deposition from a monodisperse suspension of particles of variable cohesiveness onto a rough substrate were performed. The influence of collision efficiency on the decay of the initial roughness in the course of deposition was studied.

## DEPOSITION ALGORITHM

The treatment of long-range transport of particles was based on the same concepts as in the model employed by Veerapaneni and Wiesner (7). Briefly, the particles were released one by one at a release line positioned 20 lattice units above the highest particle in the deposit at a random horizontal position along the substrate. Upon release, the particles followed a biased random walk; i.e., the probabilities for the particle to move in eight possible directions were sampled from the nonuniform probability distribution determined by a force balance on the particle. A pseudo-Peclet number was used to estimate the relative importance of diffusive and deterministic forces acting on a particle,

$$N_{Pe} = \frac{V_g + V_{pf}}{V_d}, \quad [1]$$

where  $V_g$ ,  $V_{pf}$ , and  $V_d$  are particle velocities due to gravity, permeate flow, and diffusion, correspondingly. Periodic boundary conditions were established in the horizontal direction and the width of the lattice was chosen to be much bigger than a characteristic lateral size of biggest deposit substructures to minimize the influence of boundaries. The simulation workspace was a square  $1000 \times 1000$  lattice.

The collision efficiency  $\alpha$  was used to model the propensity of particles in suspension to attach to the deposit upon contact. Therefore, attachment followed a sequence of possible contact events. The attachment was allowed to *active* sites only, i.e., the sites which were nearest neighbors of occupied sites. In the model, attaching particles do not change the arrangement of already deposited particles and, once attached, are considered to be permanently and rigidly deposited—neither resuspension nor “rolling” follows.

In this work, a collision which did not result in attachment was followed by detachment of the particle in a direction determined by the local structure of the deposit and a force balance on the particle. In the model, detachment onto active sites, onto sites occupied by deposited particles, and onto “obstructed” sites was forbidden. An “obstructed” site was a site that would only be accessible by passing through two diagonally adjacent sites. For the rest of the lattice sites available for a particle to move to from the site of the “unsuccessful” collision, the probability distribution was calculated from the force balance, which was assumed to be the same as for the free particle in the suspension. After the detachment, the particle was allowed to continue its biased random walk until the next collision.

The following assumptions were made in the model: (a) monodisperse suspension, (b) spherical particles, (c) no restructuring (here, restructuring means only breakup and compaction of the deposit under the influence of external forces or its own weight), and (d) simplistic attachment–detachment rules.

The profile of the starting surface was represented by the function

$$A_i = A_m \cos^2\left(\frac{2\pi n_w i}{L'}\right), \quad [2]$$

where

$A_i$  is amplitude of the substrate roughness at the  $i$ th location along the substrate (in units of particle diameters),

$L' = L + 2$ , where  $L$  is length of the substrate (in units of particle diameters), and 2 was needed to impose boundary conditions,  
 $l$  is location along the substrate ( $l = 1, 2, \dots, L'$ ),  
 $A_m$  is maximum amplitude of the substrate roughness (in units of particle diameters), and  
 $n_w$  is number of waves in the substrate profile of length  $L'$ .

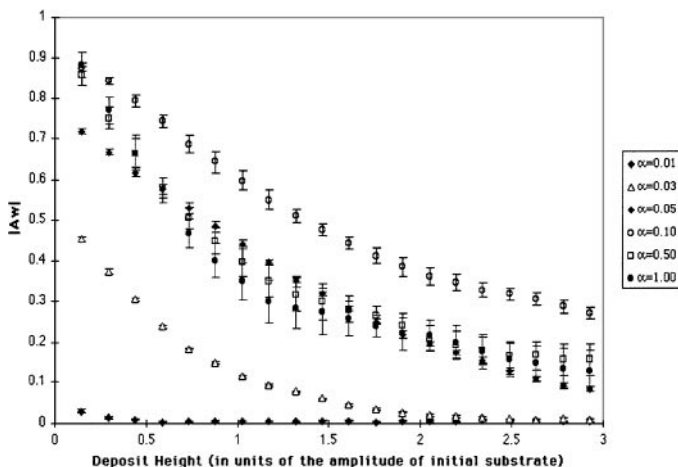
## RESULTS AND DISCUSSION

All the simulations used the parameters  $N_{pe} = 4 \times 10^{-3}$ ,  $d_p/A_m = 10^{-2}$ ,  $n_w/L = 4/1000$ , where  $d_p$  is particle diameter. The deposit profiles, i.e., contours of the upper surface of deposits, were recorded 100 times in the course of a simulation run. Fourier transform spectra were calculated for each of the profiles using the *fft* function from the MATLAB Signal Processing Toolbox. *fft(x)* returns the discrete Fourier transform of the vector  $x$  computed, in our case, with a mixed-radix fast Fourier transform algorithm (8). The 0th frequency component was subtracted from all the spectra. We considered  $A_w$  to be indicative of the deposit's "memory" of the substrate morphology.

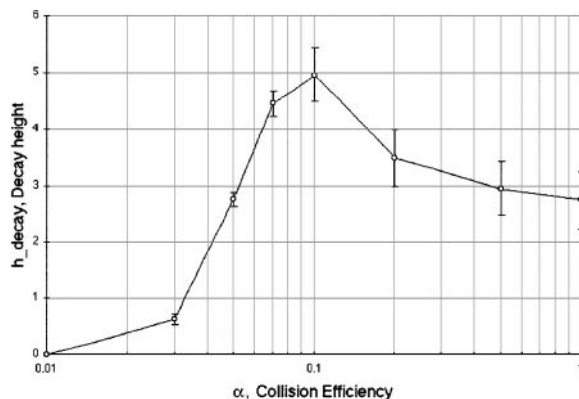
Five runs of the deposition program were done for each of the following eight values of collision efficiency  $\alpha$ : 0.01, 0.03, 0.05, 0.07, 0.10, 0.20, 0.50, 1.00. The dependence of the Fourier amplitude  $A_w$  on the deposit height is shown in Fig. 1. The values were normalized by the initial value of  $A_w$ , which corresponds to the substrate with no deposit on it. Each of these curves were fit with an exponential function  $A_w = e^{-kH_d}$ , where  $H_d$  is the height of the deposit, and  $k$  is the decay coefficient. A logarithmic fit was used to approximate the function. From these fits the values of the decay coefficient  $k \pm \delta k$  were found, where  $\delta k$  corresponds to a 95% confidence interval. We chose the value reciprocal to  $k$ ,  $h_{decay}$ , i.e., the height at which  $A_w$  decreases by a factor of  $e = 2.727$ , to represent how well the deposits preserved the initial profile of the substrate. The dependence of  $h_{decay}$  on the collision efficiency of particles is represented in Fig. 2.

As can be seen, the deposits formed from particles with intermediate values of collision efficiency  $\alpha_{opt} = 0.1$  have the best "memory" for the substrate. As expected, near-surface transport of noncohesive particles leads to a quick leveling off of initial roughness. At another extreme, values of  $\alpha$  close to 1 (immediate attachment limit), the branches of the deposit coalesce at relatively low deposit heights which also limits the influence of boundary conditions on the surface morphology of the deposit. We expect that for a smaller  $N_{pe}$  values, the  $\alpha_{opt}$  would be less, as the interaction between growing deposit branches would be enhanced.

It should be noted also, that colloids are rarely perfectly cohesive, unless the suspension is pretreated, and collision efficiencies for naturally occurring cohesive colloids are more typical in the range 0.1–1 (9).



**FIG. 1.** Decay of the  $A_0$  component of the deposit profile Fourier transform in the course of the deposit growth as a function of collision efficiency  $\alpha$ .



**FIG. 2.** Decay height as a function of collision efficiency  $\alpha$ .

## SUMMARY AND CONCLUSIONS

Knowledge of effects of long-range transport and collision efficiency of depositing particles on the connection between profile of the initial surface and morphology of the deposited layer can provide better understanding and control over many natural and engineered processes involving deposition.

In the case of diffusively depositing particles studied here, it was found that the slowest decay of a Fourier component correspondent to the roughness of initial substrate is achieved at intermediate values of  $\alpha_{opt}$  ( $\sim 0.1$ ) of collision efficiency. Lower values of  $\alpha_{opt}$  are expected for lower  $N_{pe}$  values, i.e., for a more diffusive long-range transport regime. This result suggests that there is a possible advantage in forming films or other deposited layers with either very stable or unstable particles when the goal is to mask irregularities of the substrate. In contrast, when it is desirable to maintain the form of the substrate, the depositing layer should be formed from particles of intermediate stability.

## ACKNOWLEDGMENTS

This work was supported in part by funding through the Gulf Coast Hazardous Substances Research Center.

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Received September 13, 2000; accepted February 14, 2001

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